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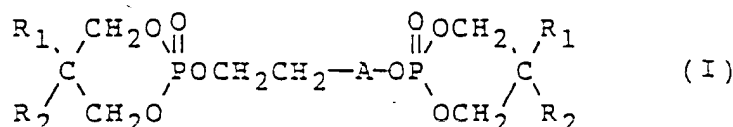
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⑤4 Organic phosphorus compounds and flame-retarded resin compositions containing the same.

(57) Organic phosphorus compounds of the formula (I):



wherein R₁ and R₂ are, the same or different, a C₁₋₈ straight chain or branched chain alkyl group, an optionally substituted C₆₋₁₂ aryl group; and A represents a bond, a lower alkylene group or -(OCH₂CH₂)_n- group, (n is an integer of 1 to 5), which are useful as flame-retardants.

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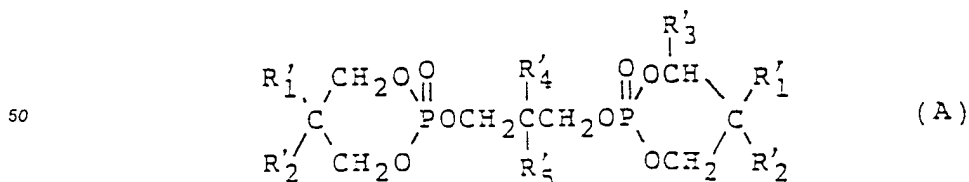
5 The present invention relates to novel organic phosphorus compounds of non-halogen type and flame-retarded resin compositions containing the same which are excellent in flame-retardant properties and heat resistance.

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As a known method for giving flame-retardant properties to organic polymers, a flame-retardant is added to organic polymers when preparing a molded product. As the flame-retardants, there are inorganic compounds, organic phosphorus compounds, organic halogen compounds and organic phosphorus compounds containing halogen. Out of the above compounds, organic halogen compounds and organic phosphorus compounds containing halogen exhibit an excellent flame-retardant effect. However, these compounds containing halogen are pyrolyzed in the process of molding resins to produce hydrogen halide, which corrodes molds and cause resins to be deteriorated and colored. Furthermore, such compounds adversely affect our working environment. Still furthermore, the compounds generate toxic gas such as hydrogen halide toxic to human bodies.

Halogen-free organic phosphorus compounds are generally used as a flame-retardant having a relatively favorable flame-retardant effect. Aromatic phosphorus compounds such as triphenyl phosphate (TPP), tricresyl phosphate (TCP) and cresyl diphenylphosphate (CDP), which are typical organic phosphorus compound, are used as a flame-retardant of each kind of engineering plastics such as phenol resin, epoxy resin and polyurethane resin or the like.

In addition, German Patent No. 3004184C2 discloses compounds of formula (A) as a flame-retardant which is added to an organic polymer such as polyolefin, polypropylene, polystyrene, ABS and polyurethane.



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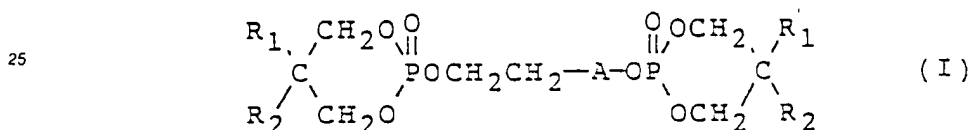
have a low heat resistance, which leads to a disadvantage of causing resins to be colored and deteriorated in the process of molding.

In recent years, the developments of plastics having high functional properties such as engineering plastics and super-engineering plastics are in progress. Since these plastics need a high molding temperature, a flame-retardant is also required to be sufficient heat resistance. As a known method for improving the heat resistance of flame-retardants, an anti-oxidant such as hindered-phenol compounds, sulfur compounds and amine compounds together with flame-retardant is added to organic polymers. However, even when such anti-oxidant is added to organic polymers, for example, together with the organic phosphorus compounds as mentioned above, coloring of resins cannot be avoided at 200 °C or more.

SUMMARY OF THE INVENTION

The present invention has been made to solve the above drawbacks of the prior art and aims to provide a novel compound which can be used as a flame-retardant for various kinds of resins, having excellent flame-retardant properties and heat resistance and good properties which do not deteriorate or corrode the resins when are mold owing to the absence of halogens, and further to provide a flame-retarded resin composition containing the above compound and a resin which is excellent in heat resistance and flame-retardant properties, last the flame-retardant properties and can form molded articles without causing dripping of molten resins.

20 Accordingly, the present invention provides an organic phosphorus compound of the formula (I) (hereinafter referred to as Compound (I)):



30 wherein R₁ and R₂ are, the same or different, a C₁₋₈ straight chain or branched chain alkyl group, or an optionally substituted C₆₋₁₂ aryl group; A represents a bond, a lower alkylene group or -(OCH₂CH₂)_n- group (n is an integer of 1 to 5) and a flame-retarded resin composition comprising Compound (I) and a resin.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an NMR spectrum of Compound 1; and
FIG. 2 is an NMR spectrum of Compound 2.

DESCRIPTION OF PREFERRED EMBODIMENTS

In the above formula (I), examples of the C₁₋₈ alkyl groups represented by R₁ and R₂ include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl, isopentyl, hexyl, 2-ethylhexyl, n-octyl, and isooctyl groups. In particular, methyl or ethyl group is preferable.

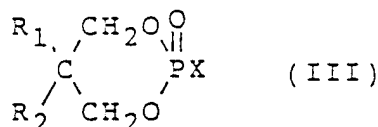
Examples of the optionally substituted C₆₋₁₂ aryl groups represented by R₁ and R₂ include phenyl, 45 cresyl, xylyl and naphthyl groups. In particular, phenyl group is preferable.

Such aryl group may be substituted with one to three C₁₋₃ alkyl groups such as methyl, ethyl and propyl.

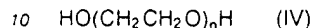
Examples of the lower alkylene groups represented by A include C₁₋₄ alkylene groups such as -CH₂-, -CH₂CH₂-, and -CH₂CH₂CH₂- groups, among which -CH₂CH₂- group is preferable.

50 Examples of $-(\text{OCH}_2\text{CH}_2)_n-$ groups represented by A are $-\text{OCH}_2\text{CH}_2-$ group (n is 1) and $-\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$ group (n is 2), among which the former is preferable.

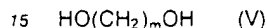
Compound (I) of the present invention can be obtained by reacting a compound of the formula (III) (hereinafter referred to as Compound (III)):



wherein R_1 and R_2 are the same meanings as described above and X is a halogen atom, with a compound of the formula (IV) (hereinafter referred to as Compound (IV)):



wherein n has the same significance as the above formula (I) or a compound of the formula (V) (hereinafter referred to as Compound (V)):



wherein m is an integer of 2 to 8 in an organic solvent in the presence of an organic base.

In the above reaction, the organic base functions as an acid acceptor. Examples of the organic bases include triethylamine, tributylamine, pyridine and dimethylaminopyridine. These bases can be used singly or as a mixture of two or more kinds. The amount of the bases to be used is 2 to 2.5 moles, preferably 2.05 to 2.2 moles, for one mole of Compound (IV).

The reaction can be conducted in an inert organic solvent such as benzene, toluene, dichloroethane, dioxane or acetonitrile or the like.

Compound (III) is used in 2 to 2.5 moles, preferably 2 to 2.1 moles, for one mole of Compound (IV).

25 The reaction can be conducted at 25 to 80°C, preferably 30 to 70°C for about two to ten hours, preferably about five to seven hours.

The reaction product can be isolated and purified by means of known methods such as solvent extraction, change of acidity or alkalinity, salting out, crystallization and recrystallization.

Out of the material compounds used in the process for preparing Compound (I), Compound (III) can be obtained by reacting phosphorus oxyhalide with a diol compound such as neopentyl glycol or the like.

30 In addition, Compound (IV) is ethylene glycol when n is 1 and diethylene glycol when n is 2. Other examples of Compound (IV) are triethylene glycol and tetraethylene glycol.

Compound (V) is ethylene glycol in case of m being 2, propylene glycol for m being 3 and butylene glycol for m being 4.

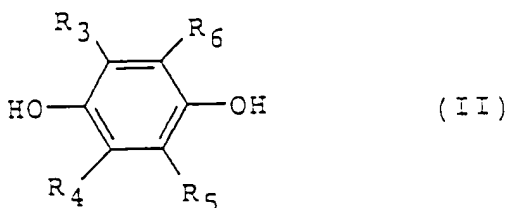
35 Compound (I) having desired phosphorus content and molecular weight can be prepared by suitably selecting the kinds and amounts of the starting Compounds (III) and (IV) in the above method. The resulting organic phosphorus Compound (I) thus obtained can be used as a flame-retardant singly or as a mixture of two or more kinds.

40 To the flame-retarded resin composition of the present invention comprises a resin and the above organic phosphorus Compound (I) optionally together with an anti-oxidant and other additives. Examples of such additives include halogen type flame-retardants, inorganic flame-retardants, antioxidants, fillers and lubricants.

45 The kind and amount of Compound (I) to be used is appropriately determined by the degree of flame-retardant properties required therein. The amount of Compound (I) to be used is 0.1 to 100 parts by weight, preferably 5 to 50 parts by weight, for 100 parts by weight of the resin. The resin, the organic phosphorus compound and the above additive when needed are kneaded and molded in accordance with the known method to give a flame-retardant molded article. Compound (I) can be added to monomers to be used in the preparation of a resin with block polymerization, a reaction mixture at the end of the block polymerization, or the resin to be subjected to molding, thereby providing flame-retardant properties thereof.

50 Examples of the above resins include thermoplastic resins such as chlorinated polyethylene, polyethylene, polypropylene, polybutadiene, polystyrene, impact-resistant polystyrene, polyvinyl chloride, ACS resin, AS resin, ABS resin, polyphenylene oxide, polymethylmethacrylate, polyamide, polyester and polycarbonate; and thermosetting resins such as polyurethane, phenolic resin, melamine resin and urea resin and unsaturated polyester. The above resins may be used singly or as a mixture.

55 The flame-retarded resin composition of the present invention may contain an anti-oxidant when required. Its examples are a hydroquinone compound of the formula (II):



10 wherein R_3 , R_4 , R_5 and R_6 are, the same or different, a hydrogen atom or a C_{1-14} straight chain or branched chain alkyl group, and known trivalent organic phosphorus compounds.

Examples of the hydroquinone compounds (II) include hydroquinone, 2, 5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone and octylhydroquinone. Preferred hydroquinone compounds having excellent heat resistance are 2,5-di-tert-amylhydroquinone and 2, 5-di-tert-butylhydroquinone.

15 Examples of the above trivalent organic compounds include triphenylphosphite, tris(nonylphenyl)-phosphite, diphenylisodecylphosphite, bis(2,4-di-tert-butylphenyl)pentaerythritoldiphosphite, tetrakis(2,4-tert-butylphenyl)4,4-diphenylenephosphonite.

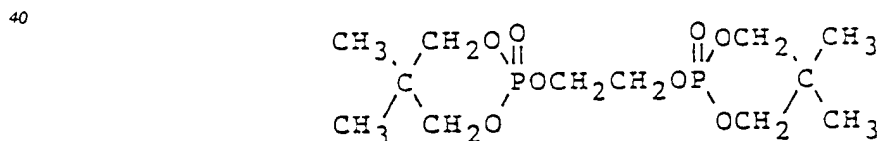
For such resins as denatured polyphenylene oxide (PPO), polystyrene or ASS resin, Compound (I) can be used together with an inorganic flame-retardant, for example, magnesium hydroxide or antimony trioxide.
20 For polyurethane foam, Compound (I) can be also used together with a non-halogen type compound such as melamine or urea.

The present invention will be detailed with respect to the following examples which are not intended for the limitation thereto. In the following examples, parts are designated in weights and temperatures in centigrades unless otherwise indicated.

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Example 1

Into a four necked flask equipped with a stirrer, a thermometer and a condenser with water scrubber was put 104 parts (1 mole) of neopentyl glycol and 100 parts of toluene, followed by addition of 153.5 parts
30 (1 mole) of phosphorus oxychloride at 50°C in an hour. The reaction was continued for 4 hours to complete dehydrochlorination. To the reaction solution was added 150g of toluene, to which 31 parts of ethylene glycol (0.5 mole) and 200 parts of dioxane were added at 20°C and further a mixture of 111 parts of triethylamine and 0.5 part of dimethylaminopyridine was dropwise added at 50°C for about 2 hours. Then the mixture was raised to 80°C and maintained for 5 hours to complete the reaction. The precipitated
35 object compound and the amine hydrochloride were collected by filtration and washed with methanol to remove the amine hydrochloride. The residue was dried in vacuo at 100°C to obtain 155g (yield: 87%) of white powder crystals. The chemical structure of the crystals is as follows (referred to as Compound 1),

mp 164 to 166°C .



The elemental analysis of Compound 1 ($C_{12}H_{24}O_8P_2$) is shown in Table 1. The NMR spectrum is also shown in FIG. 1.

50 Example 2

White crystalline powders having the following chemical structure (referred to Compound 2) were prepared in the same manner as Example 1 except that 51 parts of diethylene glycol were used in place of 31 parts of ethylene glycol. The yield was 161g (80%).

55 mp 116°C .

The elemental analysis of Compound 2 ($C_{14}H_{28}O_9P_2$) is shown in Table 1. FIG. 2 shows the NMR spectrum of Compound 2.



mp 127°C.

15 The elemental analysis of Compound 3 ($C_{14}H_{28}O_8P_2$) is shown in Table 1.



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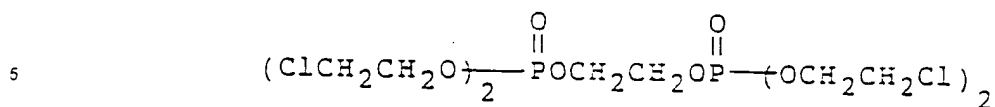
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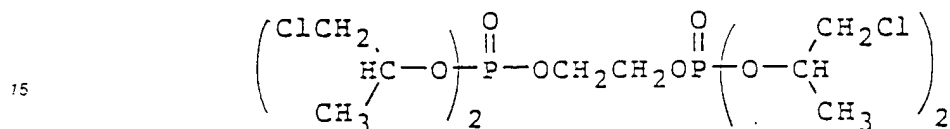
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Compound A (described in Japanese Unexamined Patent Publication No. 49-62424)



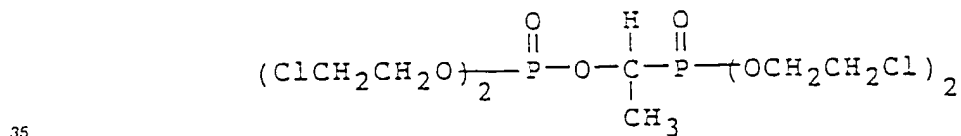
10 Compound B



20 Compound C



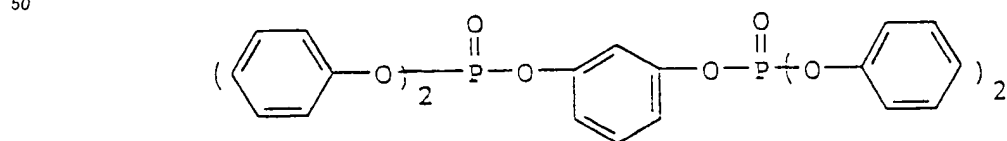
30 Compound D



40 Compound E



50 Compound F



Example 4

Flame-Retarded Resin Composition	
Polyol (manufactured by Mitsui Toatsu Chemicals, Inc., Trade name of MN-3050 ONE)	100 parts
Isocyanate (manufactured by Mitsui Toatsu Chemicals, Inc., Trade name of TDI 80/20)	55.1 parts
Polyol silicone oil (manufactured by Nihon Yunka Co., Ltd., Trade name of L-520)	1.2 parts
Tin catalyst	0.25 part
Amine catalyst	0.15 part
Water	4.5 parts
Methylene chloride	3.0 parts
Flame-retardant compound	(predetermined amount shown in Table 1)

The above ingredients were used to prepare a soft urethane foam in accordance with the one-shot method as follows.

Firstly, the polyol, silicone oil, catalysts, methylene chloride, water and flame-retardant compound were blended and homogenously mixed for a minute with a stirrer of 3000rpm. Then the isocyanate was added thereto, stirred for 5 to 7 seconds at 3000rpm and quickly poured into a box with a square-shaped cross section. Immediate foaming occurred to give the maximum volume several minutes later. The product was cured for 30 minutes in a furnace at 120 °C. The resulted foam has white and soft open cells.

Each of the resulted foams was cut to obtain a specimen, which was subjected to a burning test using MVSS-302. Furthermore a fresh specimen was treated for 3 minutes in a microwave oven (500W) followed by heating for 2 hours at 140 °C. The specimen was observed on change of color (presence or absence of scorch).

Its result is shown in Table 2 and Table 3. In the item "scorch" in Table 3, mark "O" designates almost no change of color while mark "x" is colored in brown.

Table 2

Flame-retardant	(pts.)	Average burning distance (mm)	(pts.)	Average burning distance (mm)	(pts.)	scorch
Compd. 1	8	NB 32.0	10	NB 22.8	20	○
Compd. 2	8	NB 37.0	10	NB 26.6	20	○
Compd. A	8	SE 39.6	10	NB 27.8	<u>20</u>	x
Compd. B	8	-----	10	SE 75.9	20	○
Compd. C	8	SE 76.0	10	SE 52.0	20	○
Compd. D	8	NB 31.0	10	NB 21.6	20	x
none	-----	burned				○
NB: Non Burn SE: Self Extinguish						

Table 3

Flame-retardant	(pts.)	scorch
Compound 1	20	○
Compound 2	20	○
Compound A	20	x
Compound B	20	○
Compound C	20	○
Compound D	20	x
none		○

As apparent from Table 2 and Table 3, the organic phosphorus compounds of the present invention give a better flame-retardant properties and do not occur any scorch, in comparison with the conventional halogen flame-retardant compounds. Even keeping the organic phosphorus compounds of the present invention at 80 °C for 14 days, they did not change the flame-retardant effect.

Example 5

To 100 parts of a mixture of impact-resistant polystyrene/PPO resin (45/55) were added 10 parts of the organic phosphorus compound described in Table 4. The mixture was uniformly blended for about 15 minutes using an V type blender with 10L, and converted into pellets using an extruding machine having internal diameter of 40mm. A predetermined specimen was prepared from the pellets using a molding machine with a capacity of 4 ounces.

The flame-retardant properties of the specimen were evaluated in accordance with the test method stipulated in UL-94. Five test pieces for each specimens were twice measured for a time from firing to extinguishment. Total times for two measurements are used as burning time and said time are averaged for five test pieces. Then the heat deformation temperature was measured in accordance with D648 in ASTM standard. Juicing phenomena of the surface of the molded article. Table 4 shows the result thereof.

Table 4

Flame-retardant	Average burning time (sec)	Heat deformation temperature (°C)	Juicing
Compd. 1	35	95.2	— none
Compd. 2	39	94.3	none
Compd. E	unextinguished	81.5	present
Compd. F	45	86.0	somewhat present

Example 6

To 100 parts of ABS resin (Sebian-V manufactured by Daicel Chemical Industry, Ltd., Japan) was added 10 parts of the organic phosphorus compound described in Table 5, 5 parts of tetrabromobisphenol A, and 2.5 parts of Sb₂O₃. The mixture was uniformly stirred for about 15 minutes using a V type blender with 10L, and converted into pellets using an extruding machine having internal diameter of 40mm. The pellets were molded into predetermined specimen with a 4 ounce molding machine.

The flame-retardant properties of the specimen were evaluated in accordance with the test method stipulated in UL-94. Five test pieces for each specimens were twice measured for a time from firing to extinguishment. Total times for two measurements are used as burning time and said time are averaged for five test pieces. Then the heat deformation temperature was measured in accordance with D648 in ASTM standard. Juicing phenomena of the surface of the molded article. Table 5 shows the results thereof.

5

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- 1.



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- 35

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DTLE OIH	
ORNUC III	
EXHOD NON	
DFR	270.05 MHz
ORSET	112.00 kHz
ORFIN	5800.0 Hz
POINT	32768
FREQD	5405.4 Hz
SCANS	16
ACQIN	3.031 sec
PD	3.969 sec
PW1	5.5 us
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EXREF	0.00 pps
DF	0.16 Hz
NIGAIN	9
OPERATOR :	

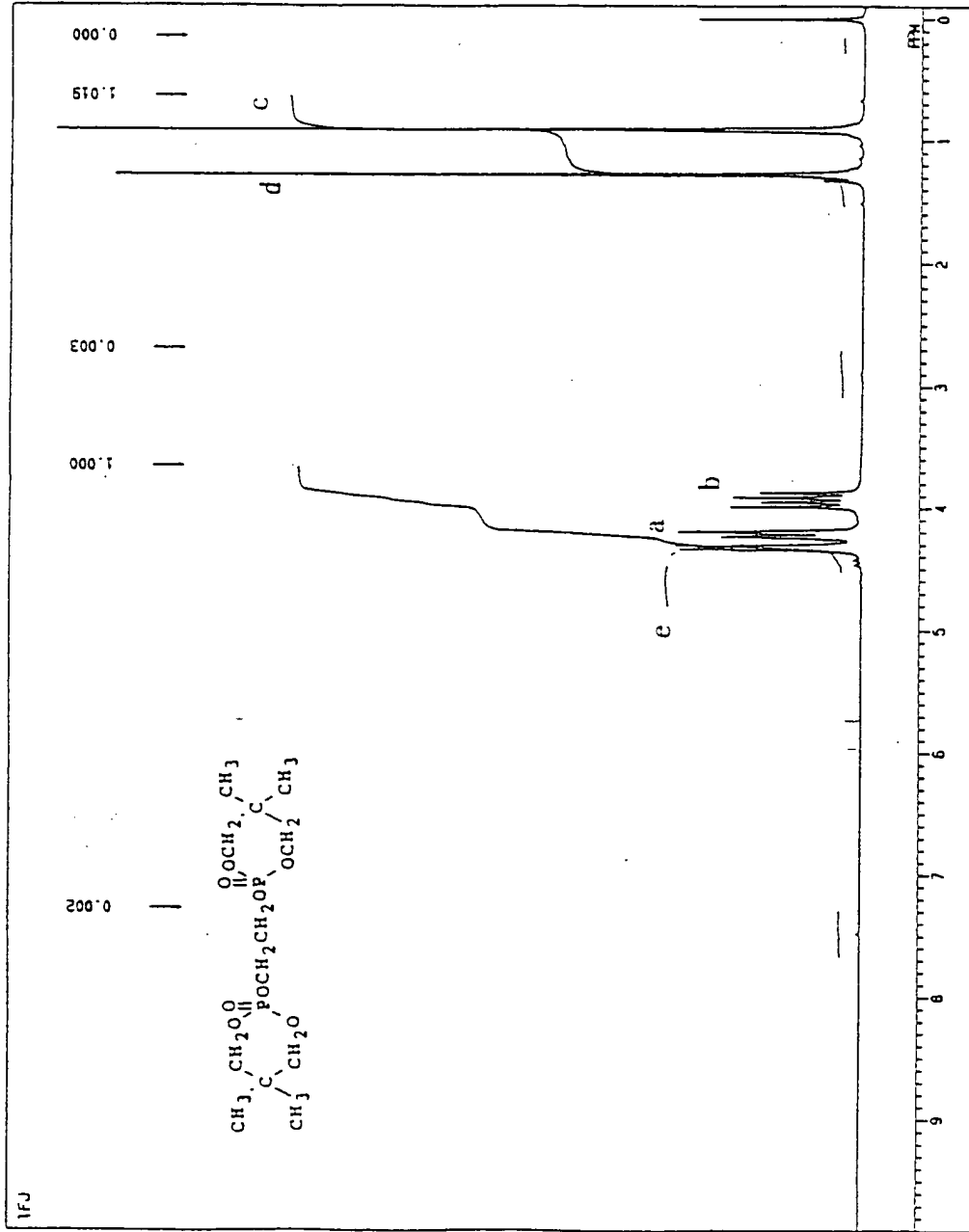
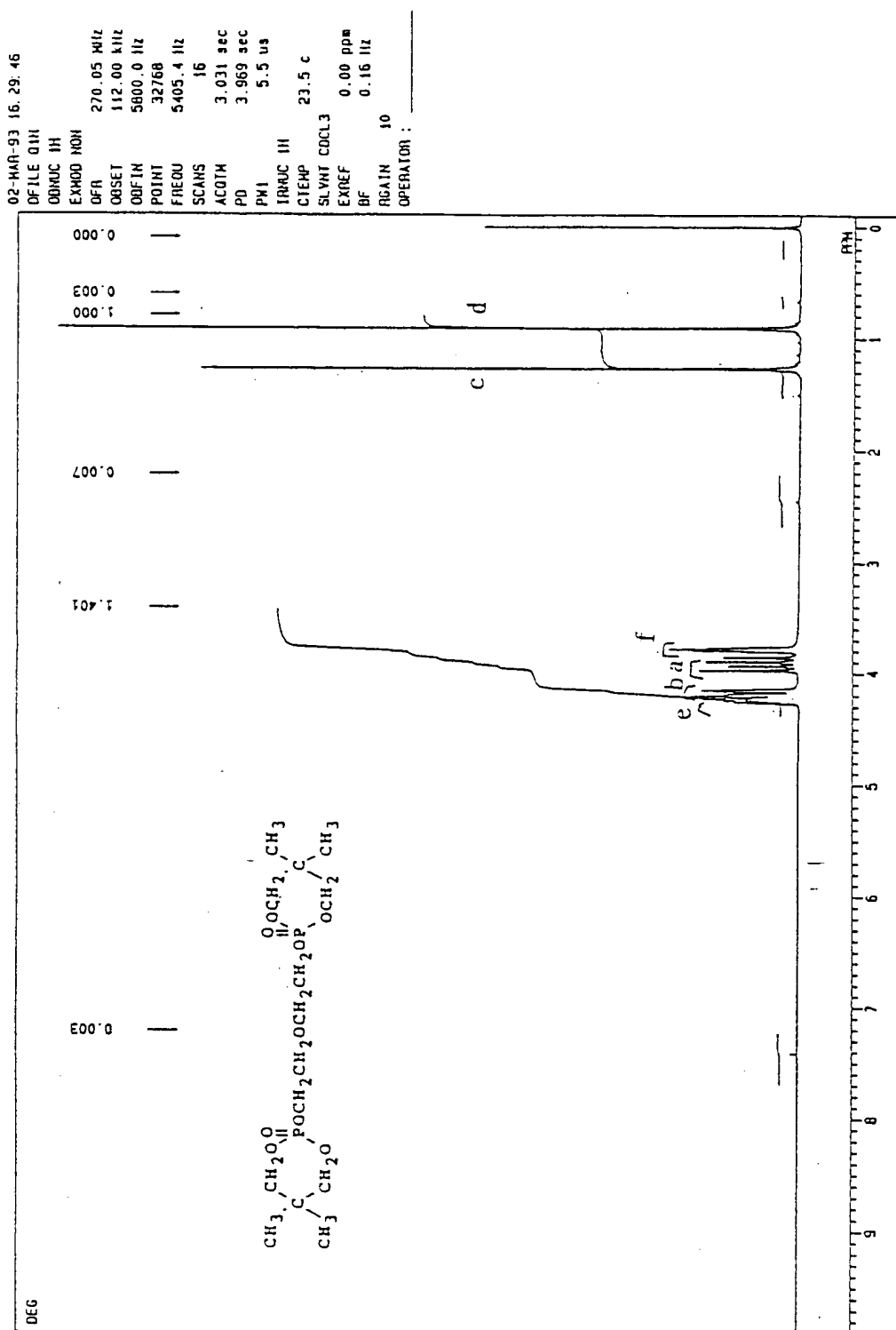


FIG 2





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 10 4004

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	PAP. - FIRE RETARD. CHEM. ASSOC. [SEMI-ANNU. MEET.] (PFRMDK);79; (INT. OPPOR. FIRE RETARD.: REGUL., NEW DEV., TOXIC.); PP.220-46 MITSUI TOATSU CHEM. INC.;CENT. RES. LAB.; JAPAN Noda E 'Phosphorus-containing flame retardants' * see particularly page 239, table 4 *	1,3,5-10	C07F9/6574 C08K5/527
X	DE-C-961 354 (UNION CARBIDE AND CARBON CORPORATION) * the whole document *	1	
D,Y	WO-A-80 01697 (SANDOZ AG) * the whole document *	1,5-10	
Y	US-A-2 952 701 (RICHARD L. MCCONNELL) * the whole document *	1,5-10	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			C07F C08K
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 13 June 1994	Examiner Beslier, L
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	